USING COMPUTATIONAL CHEMISTRY TO DESIGN A PUMP-PROBE SCHEME FOR MEASURING NITROBENZENE RADICAL CATION DYNAMICS

HUGO A. LÓPEZ PEÑA, DERRICK AMPADU BOATENG, SHANE L. McPHERSON, KATHARINE MOORE TIBBETTS, *Department of Chemistry, Virginia Commonwealth University, Richmond, Virginia, USA*.

Nitrobenzene is often used as a model molecule for the study of the dissociation dynamics of nitroaromatic energetic materials. The potential energy surfaces for the ground cationic state D_0 and the first ten excited states D_1 through D_{10} were calculated as a function of the C–NO_2 torsional angle using time-dependent density functional theory. These surfaces were employed in the prediction of the most efficient probe wavelength for femtosecond time-resolved mass spectrometry measurements. It was found that the $D_0 \rightarrow D_4$ transition in nitrobenzene cation has a geometry-dependent oscillator strength, reaching a maximum at 90° C–NO_2 torsional angle, with a corresponding energy gap of $\sim$2 eV. These results are consistent with the experimental observation of a vibrational wave packet along the C–NO_2 torsional mode in nitrobenzene cation. Time-resolved measurements using a probe wavelength of 650 nm, nearly resonant with the strong $D_0 \rightarrow D_4$ transition, result in enhanced ion yield oscillation amplitudes as compared to excitation with the nonresonant 800 nm wavelength. These results demonstrate that computational chemistry can predict the best choice of probe wavelength in time-resolved measurements of vibrational coherent states in molecular cations.